

COLLISIONAL EXCITATION OF AN ASYMMETRIC ROTOR, SILICON DICARBIDE

AMEDEO PALMA

Chemistry Department, Columbia University; Goddard Space Flight Center, Institute for Space Studies

AND

SHELDON GREEN

NASA/Goddard Space Flight Center, Institute for Space Studies

Received 1986 August 5; accepted 1986 October 24

ABSTRACT

We have computed rotational excitation rates for the asymmetric top molecule SiC₂ in collisions with low-energy He atoms. The intermolecular forces were obtained from an electron gas model, and collision dynamics were treated within the infinite-order sudden approximation. Total excitation rates, i.e., summed over final levels, are expected to be accurate to ~50%, and the larger state-to-state rates are likely to be within a factor of ~2 of the correct values, although some of the smaller (and less important) rates may be less accurate. These rates are also thought to reflect, within this level of accuracy, rates for excitation by collisions with H₂ molecules.

Subject heading: molecular processes

I. INTRODUCTION

Radio frequency and microwave observations of trace molecular components provide an important probe of physical conditions in the interstellar gas. In most of the observed regions, the relative populations among molecular rotational levels—and hence the relative intensities of different spectral lines—are determined by competition between collisional excitation and spontaneous radiative decay. Knowledge of these molecular rates is needed to interpret observations in terms of local conditions such as density and kinetic temperature. Early studies were confined mainly to linear molecules which have a simple ladder of rotational levels at energies $E_J = BJ(J + 1)$ and successive spectral transitions at frequencies $\nu = 2BJ$, where B is the rotation constant and J is the rotational quantum number. More complex molecules can be better probes insofar as their rotational levels and spectral lines are more densely spaced in energy and frequency; the symmetric top, methyl cyanide, is a good example (Cummins *et al.* 1983). Asymmetric tops might be expected to be even more useful probes.

An impediment to using more complex rotors as radioastronomical probes has been lack of the required collision rates, which are more difficult to obtain than for linear rotors. Because of the special nature of symmetric tops, some useful information can be obtained with only a crude estimate for the collision rates, although accurate values are required for quantitative analysis (Green 1986b). For the general asymmetric top, reasonable estimates for the entire matrix of state-to-state rates are needed. Obtaining these rates is particularly timely because there is now an accumulating body of observational data for several species, including SO₂, SiC₂, and the recently discovered C₃H₂. We present here results for SiC₂ using theoretical techniques that have proved useful for simpler species, modified as necessary to treat asymmetric rigid rotors.

II. DETAILS OF CALCULATION

The theoretical description of collisional excitation is conveniently divided into two parts: calculation of the interaction forces or potential energy surface, and calculation of collision

dynamics on this surface. Approximations are needed for both of these to reduce computations to a manageable size. In the interstellar gas the most important collision partner is H₂, with He being less abundant by a factor of ~5, and the most severe approximation in this study is to consider only He-SiC₂ collisions. However, based on theoretical arguments and on studies of other species, it appears that excitation by H₂ is not too different from excitation by He (Billing and Diercksen 1985; Flower and Launay 1985; Schinke *et al.* 1985).

The interaction between SiC₂ and He was obtained within the Gordon and Kim (1972) electron gas model. The electron charge densities which are required for this method were taken from Hartree-Fock calculations using a Gaussian orbital basis set of "double-zeta plus polarization" quality for SiC₂ and an accurate Slater orbital basis set for He. Although the electron gas method has known shortcomings, it is much less expensive than more rigorous ab initio methods, and it does give a reasonable description of the forces at play in rotational excitation.

The SiC₂ molecular geometry is described, in center-of-mass coordinates, by Si (0.0, 0.0, 1.5040) and C(0.0, ±1.1981, -1.7547), with distances in atomic units ($1 a_0 = 1$ Bohr radius = 5.292×10^{-11} m). The interaction energy was obtained for the He atom at several positions relative to the SiC₂, described in standard polar coordinates, with θ measured from the z-axis and ϕ measured from the x-z plane of symmetry, as $\theta = 0^\circ, 30^\circ, 45^\circ, 70^\circ, 80^\circ, 90^\circ, 110^\circ, 135^\circ, 150^\circ$, and 180° ; $\phi = 0^\circ, 30^\circ, 45^\circ, 60^\circ$, and 90° , and $R = 4.0(0.5)10.0a_0$. The angle dependence at each distance was expanded in spherical harmonics

$$V(R, \theta, \phi) = \sum_{LM} v_{LM}(R) [Y_{L,M}(\theta, \phi) + (-1)^M Y_{L,-M}(\theta, \phi)] / (1 + \delta_{M0}). \quad (1)$$

The v_{LM} were obtained by minimizing the rms relative deviations from computed points, and retaining the 24 terms with $L \leq 9$ and $M \leq 4$ gave errors of less than 8% at all distances. Continuous radial functions and derivatives were obtained by fifth-order polynomial interpolation between computed points (Green 1977).

Only a few scattering calculations have been done to date for asymmetric rotors: H₂CO-He (Garrison, Lester, and Miller 1976), but these can be simplified, since H₂CO is very nearly a symmetric top (Green *et al.* 1978); and H₂O (Green 1980a). H₂CO and H₂O are relatively light molecules, with only a few energy levels accessible at interstellar temperatures; it was therefore possible to perform coupled channel calculations for both. Because of the many levels accessible in a heavier system such as SiC₂, such calculations are not feasible. However, in that case the simple infinite-order sudden approximation (IOSA), which ignores the energy splitting compared with the collision energy, becomes reliable. IOSA formalism for asymmetric rotors was discussed briefly by Green (1979). As this is the first application of this formalism, we review it here in some detail.

Wave functions for asymmetric top rotors can be expanded in terms of symmetric top eigenfunctions:

$$|j\tau m\rangle = \sum_k a_k^{j\tau} |jkm\rangle, \quad (2)$$

where j is the total angular momentum with projection m on a space-fixed axis, k is the projection of j on the symmetry axis (and is a good quantum number in the case of a symmetric top), and τ is an index that labels the asymmetric top functions. Since k takes the $2j+1$ values from $-j$ to $+j$, there will be $2j+1$ values of τ as well.

The expansion coefficients, $a_k^{j\tau}$, are obtained by solving a standard secular equation

$$\sum_k a_k^{j\tau} [\langle jkm | H_{\text{rot}} | j'k'm' \rangle - E_{j\tau} \delta_{k,k'}] = 0, \quad (3)$$

where the rotational Hamiltonian is

$$H_{\text{rot}} = (2I_x)^{-1} J_x^2 + (2I_y)^{-1} J_y^2 + (2I_z)^{-1} J_z^2. \quad (4)$$

Here I_α and J_α are the moment of inertia and angular momentum operator about the α -axis; note that these axes must correspond to those used to define the interaction potential (cf. eq. [1]).

It is possible by symmetry to block-diagonalize $\langle jkm | H_{\text{rot}} | j'k'm' \rangle$. First, even k and odd k do not mix; for a given $j\tau$ the $a_k^{j\tau}$ will be nonzero for only even k or only odd k . Further simplification obtains by transforming to a basis composed of symmetric and antisymmetric combinations of $|jkm\rangle$ and $|j-km\rangle$; the $a_k^{j\tau}$ will thus satisfy

$$a_{-k}^{j\tau} = \epsilon_{j\tau} a_k^{j\tau}, \quad (5)$$

where $\epsilon_{j\tau} = \pm 1$ for a given rotor function.

Silicon dicarbide is not too far from a symmetric top limit; its asymmetry parameter is $\kappa = -0.87$, compared with the prolate symmetric top limit of $\kappa = -1.0$. Therefore, its rotational levels can be labeled by the almost good k quantum number. Levels with $k > 0$ are split into doublets with the lower member corresponding to $\epsilon_{j\tau} = +1$. Although little error would be introduced in the rate constants by treating SiC₂ as a near symmetric top, we have retained the full asymmetric top formalism in the present study. Because of spin statistics for the identical carbon nuclei, the wave functions vanish for odd values of k , and these levels are not observed. Eigenvectors, i.e., $a_k^{j\tau}$, are presented in Table 1 for some of the lower rotational levels.

In the IOSA the molecular rotation is "frozen" during a collision, and one solves a standard "central potential" scattering equation to obtain the phase shift or S -matrix, which then depends parametrically on the angles of orientation of the

TABLE 1
ASYMMETRIC TOP ROTOR EIGENFUNCTIONS FOR SiC₂

| $j\tau$ | $E_{j\tau}/\text{GHz}$ | $\epsilon_{j\tau}$ | $a_0^{j\tau}$ | $a_2^{j\tau}$ | $a_4^{j\tau}$ | $a_6^{j\tau}$ |
|-----------------------|------------------------|--------------------|---------------|---------------|---------------|---------------|
| 0 ₀₀ | 0.0 | + | +1.00000 | ... | ... | ... |
| 1 ₀₁ | 23.60 | + | +1.00000 | ... | ... | ... |
| 2 ₀₂ | 70.68 | + | +0.99958 | +0.02041 | ... | ... |
| 2 ₂₁ | 233.16 | - | 0.0 | +0.70711 | ... | ... |
| 2 ₂₀ | 233.30 | + | -0.02886 | +0.70681 | ... | ... |
| 3 ₀₃ | 140.95 | + | +0.99794 | +0.04541 | ... | ... |
| 3 ₂₂ | 303.97 | - | 0.0 | +0.70711 | ... | ... |
| 3 ₂₁ | 304.65 | + | -0.06422 | +0.70565 | ... | ... |
| 4 ₀₄ | 234.03 | + | +0.99394 | +0.07774 | 0.00086 | ... |
| 4 ₂₃ | 398.28 | - | 0.0 | +0.70703 | 0.01040 | ... |
| 4 ₂₂ | 400.29 | + | -0.10994 | +0.70274 | 0.01038 | ... |
| 4 ₄₁ | 885.55 | - | 0.0 | -0.01040 | 0.70703 | ... |
| 4 ₄₀ | 885.55 | + | +0.00041 | -0.01041 | 0.70703 | ... |
| 5 ₀₅ | 349.43 | + | +0.98641 | +0.11616 | 0.00250 | ... |
| 5 ₂₄ | 516.00 | - | 0.0 | +0.70681 | 0.02041 | ... |
| 5 ₂₃ | 520.62 | + | -0.16431 | +0.69720 | 0.02032 | ... |
| 5 ₄₂ | 1003.87 | - | 0.0 | -0.02041 | 0.70681 | ... |
| 5 ₄₁ | 1003.87 | + | +0.00124 | -0.02046 | 0.70681 | ... |
| 6 ₀₆ | 486.64 | + | +0.97452 | +0.15853 | 0.00536 | 0.00004 |
| 6 ₂₅ | 657.01 | - | 0.0 | +0.70637 | 0.03222 | 0.00027 |
| 6 ₂₄ | 677.04 | + | -0.22430 | +0.68835 | 0.03198 | 0.00027 |
| 6 ₄₃ | 1145.95 | - | 0.0 | -0.03222 | 0.70631 | 0.00958 |
| 6 ₄₂ | 1145.96 | + | +0.00276 | -0.03237 | 0.70630 | 0.00958 |

rotor as well as on the usual partial wave, i.e., $S^l(\theta, \phi)$. State-to-state S -matrix elements are obtained as $\langle j\tau m | S^l(\theta, \phi) | j'\tau' m' \rangle$. It is convenient to expand the orientation dependence of the IOSA S -matrices in a manner similar to that used for the potential,

$$S^l(\theta, \phi) = \sum_{LM} S_{LM}^l Y_{LM}(\theta, \phi). \quad (6)$$

Computationally, the S_{LM}^l are obtained using the orthogonality properties of spherical harmonics and two-dimensional Gauss quadratures. It is convenient to further define "generalized IOSA cross sections" which are summed over partial waves

$$Q(L, M, M' | E) = (2\pi\mu/E) \sum_l (2l+1) \times [(4\pi)^{-1} S_{LM'}^l * S_{LM}^l - \delta_{L0}], \quad (7)$$

where E is the collision energy and μ is the reduced mass. All the state-to-state cross sections can be computed in terms of the $Q(L, M, M')$ as

$$\sigma(j\tau \rightarrow j'\tau' | E) = (2j'+1) \times \sum_{L,M,M'} C(j, \tau, j', \tau' | L, M, M') Q(L, M, M' | E), \quad (8)$$

where the "spectroscopic coefficients" contain all information about the rotational wavefunctions:

$$C(j, \tau, j', \tau' | L, M_p, M_q) = \sum_{p,p',q,q'} a_p^{j\tau} a_q^{j\tau} a_{p'}^{j'\tau'} a_{q'}^{j'\tau'} (-1)^{p'+q'} \begin{pmatrix} j & L & j' \\ -p & M_p & p' \end{pmatrix} \begin{pmatrix} j & L & j' \\ -q & M_q & q' \end{pmatrix} \quad (9)$$

When the potential is symmetric with respect to reflection in the (x, z) -plane (as is the case here),

$$Q(L, M, M') = Q(L, M', M)^*. \quad (10)$$

Further, owing to symmetries of the $a_k^{j\tau}$, $C(L, M, M') = C(L, M', M)$, so that only the real part of $Q(L, M, M')$ is required, and the cross sections are real.

TABLE 2
GENERALIZED IOS RATES ($\text{cm}^3 \text{s}^{-1}$) FOR $\text{SiC}_2\text{-He}$ COLLISIONS

| L | M | M' | Temperature | | | | | Temperature | | | | | | | |
|---|---|----|-------------|-------------|-------------|-------------|-------------|-------------|---|----|-------------|-------------|-------------|-------------|-------------|
| | | | 25 K | 50 K | 75 K | 100 K | 125 K | L | M | M' | 25 K | 50 K | 75 K | 100 K | 125 K |
| 1 | 0 | 0 | 1.86 (-11) | 2.18 (-11) | 2.29 (-11) | 2.36 (-11) | 2.41 (-11) | 8 | 4 | 0 | 2.12 (-13) | 8.92 (-13) | 1.79 (-12) | 2.66 (-12) | 3.41 (-12) |
| 2 | 0 | 0 | 5.10 (-11) | 7.14 (-11) | 8.10 (-11) | 8.70 (-11) | 9.14 (-11) | 8 | 4 | 2 | 9.28 (-16) | -1.53 (-13) | -4.11 (-13) | -6.91 (-13) | -9.56 (-13) |
| 2 | 2 | 0 | -1.16 (-11) | -1.43 (-11) | -1.55 (-11) | -1.63 (-11) | -1.70 (-11) | 8 | 4 | 4 | 1.15 (-13) | 5.02 (-13) | 1.03 (-12) | 1.55 (-12) | 2.02 (-12) |
| 2 | 2 | 2 | 3.23 (-12) | 4.03 (-12) | 4.55 (-12) | 5.02 (-12) | 5.45 (-12) | 8 | 6 | 0 | -3.39 (-14) | -3.08 (-13) | -6.75 (-13) | -1.02 (-12) | -1.32 (-12) |
| 3 | 0 | 0 | 1.39 (-11) | 1.99 (-11) | 2.26 (-11) | 2.41 (-11) | 2.50 (-11) | 8 | 6 | 2 | 6.65 (-15) | -3.41 (-15) | -6.17 (-15) | -5.37 (-15) | -2.78 (-15) |
| 3 | 2 | 0 | 3.71 (-12) | 4.86 (-12) | 5.28 (-12) | 5.47 (-12) | 5.59 (-12) | 8 | 6 | 4 | -1.09 (-14) | -1.42 (-13) | -3.19 (-13) | -4.89 (-13) | -6.39 (-13) |
| 3 | 2 | 2 | 3.55 (-12) | 5.11 (-12) | 5.91 (-12) | 6.43 (-12) | 6.82 (-12) | 8 | 6 | 6 | 1.81 (-14) | 6.59 (-14) | 1.36 (-13) | 2.06 (-13) | 2.69 (-13) |
| 4 | 0 | 0 | 5.42 (-12) | 1.26 (-11) | 1.76 (-11) | 2.10 (-11) | 2.33 (-11) | 9 | 0 | 0 | 3.97 (-13) | 1.10 (-12) | 2.22 (-12) | 3.37 (-12) | 4.44 (-12) |
| 4 | 2 | 0 | -4.47 (-12) | -9.21 (-12) | -1.22 (-11) | -1.41 (-11) | -1.55 (-11) | 9 | 2 | 0 | -2.28 (-13) | -3.16 (-13) | -4.04 (-13) | -4.49 (-13) | -4.57 (-13) |
| 4 | 2 | 2 | 4.08 (-12) | 7.43 (-12) | 9.38 (-12) | 1.06 (-11) | 1.15 (-11) | 9 | 2 | 2 | 1.70 (-13) | 2.80 (-13) | 4.75 (-13) | 7.00 (-13) | 9.25 (-13) |
| 4 | 4 | 0 | 1.36 (-12) | 2.31 (-12) | 2.74 (-12) | 2.95 (-12) | 3.07 (-12) | 9 | 4 | 0 | -5.12 (-13) | -8.10 (-13) | -1.39 (-12) | -2.04 (-12) | -2.65 (-12) |
| 4 | 4 | 2 | -1.29 (-12) | -2.08 (-12) | -2.45 (-12) | -2.67 (-12) | -2.81 (-12) | 9 | 4 | 2 | 3.42 (-13) | 2.77 (-13) | 1.92 (-13) | 8.33 (-14) | -3.85 (-14) |
| 4 | 4 | 4 | 5.15 (-13) | 7.55 (-13) | 8.92 (-13) | 9.89 (-13) | 1.07 (-12) | 9 | 4 | 4 | 9.35 (-13) | 1.00 (-12) | 1.31 (-12) | 1.73 (-12) | 2.18 (-12) |
| 5 | 0 | 0 | 8.28 (-12) | 1.68 (-11) | 2.23 (-11) | 2.58 (-11) | 2.81 (-11) | 9 | 6 | 0 | 5.74 (-14) | 2.54 (-13) | 5.57 (-13) | 8.67 (-13) | 1.15 (-12) |
| 5 | 2 | 0 | 2.62 (-12) | 5.67 (-12) | 7.79 (-12) | 9.23 (-12) | 1.02 (-11) | 9 | 6 | 2 | -2.54 (-14) | -6.99 (-14) | -1.34 (-13) | -1.96 (-13) | -2.49 (-13) |
| 5 | 2 | 2 | 1.69 (-12) | 4.12 (-12) | 6.08 (-12) | 7.55 (-12) | 8.68 (-12) | 9 | 6 | 4 | -5.08 (-14) | -1.38 (-13) | -2.92 (-13) | -4.64 (-13) | -6.30 (-13) |
| 5 | 4 | 0 | -1.13 (-12) | -2.55 (-12) | -3.48 (-12) | -4.09 (-12) | -4.51 (-12) | 9 | 6 | 6 | 1.52 (-14) | 7.12 (-14) | 1.63 (-13) | 2.63 (-13) | 3.58 (-13) |
| 5 | 4 | 2 | -3.99 (-13) | -1.10 (-12) | -1.61 (-12) | -1.99 (-12) | -2.26 (-12) | 10 | 0 | 0 | 2.53 (-13) | 1.34 (-12) | 3.20 (-12) | 5.31 (-12) | 7.39 (-12) |
| 5 | 4 | 4 | 3.13 (-13) | 5.49 (-13) | 7.12 (-13) | 8.27 (-13) | 9.13 (-13) | 10 | 2 | 0 | 3.69 (-14) | 3.23 (-13) | 7.29 (-13) | 1.13 (-12) | 1.49 (-12) |
| 6 | 0 | 0 | 5.70 (-13) | 2.05 (-12) | 3.54 (-12) | 4.77 (-12) | 5.73 (-12) | 10 | 2 | 2 | 5.66 (-14) | 2.28 (-13) | 4.67 (-13) | 7.12 (-13) | 9.38 (-13) |
| 6 | 2 | 0 | -3.61 (-13) | -1.73 (-12) | -3.20 (-12) | -4.43 (-12) | -5.40 (-12) | 10 | 4 | 0 | -8.79 (-15) | 2.33 (-13) | 7.01 (-13) | 1.29 (-12) | 1.91 (-12) |
| 6 | 2 | 2 | 1.11 (-12) | 3.12 (-12) | 5.01 (-12) | 6.53 (-12) | 7.73 (-12) | 10 | 4 | 2 | 1.88 (-14) | -2.37 (-16) | -4.04 (-14) | -9.12 (-14) | -1.45 (-13) |
| 6 | 4 | 0 | 3.80 (-13) | 1.21 (-12) | 1.98 (-12) | 2.58 (-12) | 3.04 (-12) | 10 | 4 | 4 | 4.45 (-14) | 1.54 (-13) | 3.96 (-13) | 7.13 (-13) | 1.06 (-12) |
| 6 | 4 | 2 | -1.57 (-13) | -8.38 (-13) | -1.49 (-12) | -2.02 (-12) | -2.45 (-12) | 10 | 6 | 0 | -2.72 (-14) | -2.49 (-13) | -6.67 (-13) | -1.17 (-12) | -1.68 (-12) |
| 6 | 4 | 4 | 2.87 (-13) | 7.91 (-13) | 1.24 (-12) | 1.58 (-12) | 1.86 (-12) | 10 | 6 | 2 | -6.35 (-15) | -4.82 (-14) | -1.17 (-13) | -1.93 (-13) | -2.66 (-13) |
| 6 | 6 | 0 | -1.00 (-13) | -3.12 (-13) | -4.78 (-13) | -5.91 (-13) | -6.70 (-13) | 10 | 6 | 4 | -7.48 (-15) | -6.84 (-14) | -1.93 (-13) | -3.52 (-13) | -5.22 (-13) |
| 6 | 6 | 2 | 1.54 (-13) | 3.41 (-13) | 4.56 (-13) | 5.23 (-13) | 5.61 (-13) | 10 | 6 | 6 | 5.26 (-15) | 5.41 (-14) | 1.53 (-13) | 3.96 (-13) | 7.13 (-13) |
| 6 | 6 | 4 | -5.76 (-14) | -1.97 (-13) | -3.12 (-13) | -3.98 (-13) | -4.64 (-13) | 11 | 0 | 0 | 2.40 (-14) | 1.79 (-13) | 4.95 (-13) | 8.82 (-13) | 1.29 (-12) |
| 6 | 6 | 6 | 3.31 (-14) | 7.55 (-14) | 1.12 (-13) | 1.42 (-13) | 1.67 (-13) | 11 | 2 | 0 | -1.71 (-14) | -7.70 (-14) | -2.05 (-13) | -3.61 (-13) | -5.22 (-13) |
| 7 | 0 | 0 | 1.62 (-12) | 5.40 (-12) | 9.21 (-12) | 1.24 (-11) | 1.49 (-11) | 11 | 2 | 2 | 2.61 (-14) | 6.20 (-13) | 1.29 (-13) | 2.06 (-13) | 2.83 (-13) |
| 7 | 2 | 0 | 1.69 (-13) | 9.55 (-13) | 1.96 (-12) | 2.88 (-12) | 3.67 (-12) | 11 | 4 | 0 | -1.77 (-14) | -1.92 (-14) | -6.98 (-14) | -1.68 (-13) | -2.91 (-13) |
| 7 | 2 | 2 | 2.01 (-13) | 8.23 (-13) | 1.66 (-12) | 2.47 (-12) | 3.20 (-12) | 11 | 4 | 2 | 3.65 (-14) | 5.42 (-14) | 9.73 (-14) | 1.51 (-13) | 2.06 (-13) |
| 7 | 4 | 0 | -6.14 (-13) | -1.95 (-12) | -3.36 (-12) | -4.55 (-12) | -5.50 (-12) | 11 | 4 | 4 | 6.82 (-14) | 1.27 (-13) | 2.84 (-13) | 5.25 (-13) | 8.18 (-13) |
| 7 | 4 | 2 | -7.04 (-14) | -4.63 (-13) | -9.58 (-13) | -1.43 (-12) | -1.83 (-12) | 11 | 6 | 0 | 1.07 (-14) | 7.30 (-14) | 2.19 (-13) | 4.13 (-13) | 6.20 (-13) |
| 7 | 4 | 4 | 2.88 (-13) | 7.80 (-13) | 1.33 (-12) | 1.81 (-12) | 2.21 (-12) | 11 | 6 | 2 | -1.34 (-14) | -4.66 (-14) | -1.18 (-13) | -2.09 (-13) | -3.04 (-13) |
| 7 | 6 | 0 | 1.98 (-13) | 6.42 (-13) | 1.05 (-12) | 1.37 (-12) | 1.61 (-12) | 11 | 6 | 4 | -1.80 (-14) | -3.91 (-14) | -1.10 (-13) | -2.23 (-13) | -3.63 (-13) |
| 7 | 6 | 2 | 4.38 (-15) | 3.83 (-14) | 7.14 (-14) | 9.53 (-14) | 1.11 (-13) | 11 | 6 | 6 | 7.99 (-15) | 4.20 (-14) | 1.31 (-13) | 2.61 (-13) | 4.13 (-13) |
| 7 | 6 | 4 | -5.05 (-14) | -1.99 (-13) | -3.39 (-13) | -4.51 (-13) | -5.39 (-13) | 12 | 0 | 0 | 7.26 (-14) | 4.32 (-13) | 1.31 (-12) | 2.62 (-12) | 4.16 (-12) |
| 7 | 6 | 6 | 3.89 (-14) | 9.65 (-14) | 1.49 (-13) | 1.91 (-13) | 2.25 (-13) | 12 | 2 | 0 | -1.42 (-14) | 4.30 (-14) | 1.73 (-13) | 3.45 (-13) | 5.33 (-13) |
| 8 | 0 | 0 | 6.05 (-13) | 2.25 (-12) | 4.23 (-12) | 6.05 (-12) | 7.57 (-12) | 12 | 2 | 2 | 1.85 (-14) | 4.20 (-14) | 7.50 (-14) | 1.11 (-13) | 1.46 (-13) |
| 8 | 2 | 0 | 2.08 (-13) | 4.60 (-13) | 5.23 (-13) | 5.48 (-13) | 5.93 (-13) | 12 | 4 | 0 | -1.93 (-14) | 1.15 (-14) | 1.08 (-13) | 2.77 (-13) | 5.02 (-13) |
| 8 | 2 | 2 | 2.61 (-13) | 9.19 (-13) | 1.69 (-12) | 2.42 (-12) | 3.04 (-12) | 12 | 4 | 2 | 1.40 (-14) | 7.54 (-15) | -4.30 (-15) | -1.47 (-14) | -2.13 (-14) |

TABLE 2—Continued

| L | M | M' | Temperature | | | | Temperature | | | | | | | | |
|----|---|----|-------------|-------------|-------------|-------------|-------------|----|------|------|-------------|-------------|-------------|-------------|-------------|
| | | | 25 K | 50 K | 75 K | 100 K | 125 K | 14 | 25 K | 50 K | 75 K | 100 K | 125 K | | |
| 12 | 4 | 4 | 1.89 (-14) | 4.23 (-14) | 1.16 (-13) | 2.37 (-13) | 3.88 (-13) | 14 | 4 | 0 | -8.09 (-15) | -1.25 (-14) | -2.38 (-14) | -4.30 (-14) | -6.61 (-14) |
| 12 | 6 | 0 | -9.50 (-15) | -8.77 (-14) | -3.23 (-13) | -7.03 (-13) | -1.17 (-12) | 14 | 4 | 2 | 6.26 (-15) | 8.24 (-15) | 9.45 (-15) | 1.38 (-14) | 2.24 (-14) |
| 12 | 6 | 2 | 6.58 (-15) | 5.22 (-15) | -3.52 (-14) | -7.88 (-14) | -1.30 (-13) | 14 | 4 | 4 | 7.10 (-15) | 1.30 (-14) | 3.21 (-14) | 6.86 (-14) | 1.19 (-13) |
| 12 | 6 | 4 | 5.59 (-15) | -6.24 (-15) | -4.35 (-14) | -1.08 (-13) | -1.93 (-13) | 14 | 6 | 0 | -3.05 (-15) | -1.78 (-14) | -9.20 (-14) | -2.49 (-13) | -4.77 (-13) |
| 12 | 6 | 6 | 6.64 (-15) | 2.62 (-14) | 9.40 (-14) | 2.12 (-13) | 3.64 (-13) | 14 | 6 | 2 | 2.75 (-15) | 4.58 (-15) | 9.70 (-15) | 2.00 (-14) | 3.50 (-14) |
| 13 | 0 | 0 | 1.47 (-14) | 1.12 (-13) | 3.87 (-13) | 8.06 (-13) | 1.30 (-12) | 14 | 6 | 4 | 2.47 (-15) | 1.55 (-15) | -3.41 (-15) | -1.29 (-14) | -2.61 (-14) |
| 13 | 2 | 0 | 1.12 (-15) | 1.26 (-14) | 3.20 (-14) | 5.36 (-14) | 7.44 (-14) | 14 | 6 | 6 | 1.73 (-15) | 6.93 (-15) | 3.47 (-14) | 9.60 (-14) | 1.88 (-13) |
| 13 | 2 | 2 | 4.49 (-15) | 2.33 (-14) | 6.03 (-14) | 1.09 (-13) | 1.62 (-13) | 15 | 0 | 0 | 6.31 (-15) | 5.89 (-14) | 2.71 (-13) | 6.83 (-13) | 1.26 (-12) |
| 13 | 4 | 0 | 3.11 (-15) | 3.77 (-14) | 1.17 (-13) | 2.26 (-13) | 3.46 (-13) | 15 | 2 | 0 | -1.13 (-15) | 8.59 (-15) | 5.06 (-14) | 1.33 (-13) | 2.50 (-13) |
| 13 | 4 | 2 | 2.77 (-15) | 1.52 (-14) | 4.76 (-14) | 9.89 (-14) | 1.62 (-13) | 15 | 2 | 2 | 1.58 (-15) | 8.73 (-15) | 2.63 (-14) | 5.56 (-14) | 9.48 (-14) |
| 13 | 4 | 4 | 3.68 (-15) | 2.32 (-14) | 7.79 (-14) | 1.70 (-13) | 2.91 (-13) | 15 | 4 | 0 | -5.28 (-16) | 1.34 (-14) | 6.54 (-14) | 1.61 (-13) | 2.90 (-13) |
| 13 | 6 | 0 | 1.66 (-15) | 1.30 (-14) | 6.69 (-14) | 1.70 (-13) | 3.07 (-13) | 15 | 4 | 2 | 7.30 (-16) | 4.84 (-15) | 1.76 (-14) | 4.11 (-14) | 7.33 (-14) |
| 13 | 6 | 2 | -2.83 (-15) | -1.18 (-14) | -3.70 (-14) | -7.63 (-14) | -1.23 (-13) | 15 | 4 | 4 | 7.89 (-16) | 5.39 (-15) | 2.02 (-14) | 4.67 (-14) | 8.23 (-14) |
| 13 | 6 | 4 | -2.37 (-15) | -6.09 (-15) | -2.16 (-14) | -5.52 (-14) | -1.05 (-13) | 15 | 6 | 0 | -1.10 (-15) | -3.09 (-15) | 2.50 (-15) | 2.46 (-14) | 6.47 (-14) |
| 13 | 6 | 6 | 3.71 (-15) | 1.40 (-14) | 5.83 (-14) | 1.47 (-13) | 2.71 (-13) | 15 | 6 | 2 | 1.55 (-16) | -1.70 (-15) | -8.37 (-15) | -1.89 (-14) | -3.07 (-14) |
| 14 | 0 | 0 | 1.64 (-14) | 8.99 (-14) | 3.46 (-13) | 8.31 (-13) | 1.50 (-12) | 15 | 6 | 4 | 3.10 (-16) | -6.94 (-16) | -3.94 (-15) | -1.02 (-14) | -1.94 (-14) |
| 14 | 2 | 0 | -8.08 (-15) | -1.49 (-14) | -3.02 (-14) | -6.08 (-14) | -1.05 (-13) | 15 | 6 | 6 | 8.05 (-16) | 3.69 (-15) | 1.95 (-14) | 5.66 (-14) | 1.15 (-13) |
| 14 | 2 | 2 | 7.50 (-15) | 1.28 (-14) | 1.78 (-14) | 2.45 (-14) | 3.39 (-14) | | | | | | | | |

NOTE.—Parentheses enclose powers of 10.

TABLE 3
STAGE-TO-STATE EXCITATION RATES ($\text{cm}^3 \text{s}^{-1}$) FOR SiC_2 AT 100 K

| final level | initial level | | | | | | | | | |
|-------------|---------------|----------|----------|----------|----------|----------|----------|----------|----------|----------|
| | 000 | 101 | 202 | 303 | 221 | 220 | 404 | 322 | 321 | 505 |
| 000 | *** | 7.9(-12) | 1.8(-11) | 3.8(-12) | 0.0 | 2.6(-12) | 2.1(-12) | 0.0 | 2.0(-12) | 0.0 |
| 101 | 2.4(-11) | *** | 1.6(-11) | 2.7(-11) | 4.4(-12) | 1.9(-12) | 1.0(-11) | 2.1(-12) | 6.4(-12) | 3.1(-12) |
| 202 | 8.6(-11) | 2.6(-11) | *** | 2.1(-11) | 5.1(-12) | 5.2(-12) | 2.9(-11) | 9.0(-12) | 2.1(-12) | 4.7(-12) |
| 303 | 2.5(-11) | 5.9(-11) | 2.9(-11) | *** | 7.3(-12) | 6.5(-12) | 2.1(-11) | 5.9(-12) | 4.7(-12) | 3.2(-11) |
| 221 | 0.0 | 6.7(-12) | 4.7(-12) | 5.0(-12) | *** | 1.7(-11) | 4.2(-12) | 1.3(-11) | 3.6(-11) | 2.5(-12) |
| 220 | 1.1(-11) | 2.9(-12) | 4.8(-12) | 4.5(-12) | 1.7(-11) | *** | 3.7(-12) | 3.3(-11) | 1.2(-11) | 3.8(-12) |
| 404 | 1.7(-11) | 2.7(-11) | 4.9(-11) | 2.6(-11) | 7.5(-12) | 6.7(-12) | *** | 5.8(-12) | 6.3(-12) | 2.0(-11) |
| 322 | 0.0 | 4.3(-12) | 1.1(-11) | 5.5(-12) | 1.7(-11) | 4.4(-11) | 4.4(-12) | *** | 1.5(-11) | 3.4(-12) |
| 321 | 1.2(-11) | 1.3(-11) | 2.6(-12) | 4.3(-12) | 4.8(-11) | 1.6(-11) | 4.8(-12) | 1.5(-11) | 1.2(-11) | 3.7(-12) |
| 505 | 3.0(-11) | 9.7(-12) | 2.3(-11) | 4.6(-11) | 5.2(-12) | 7.9(-12) | 2.3(-11) | 5.2(-12) | 5.6(-12) | *** |
| 423 | 0.0 | 4.2(-12) | 7.3(-12) | 1.3(-11) | 2.5(-11) | 1.6(-11) | 4.0(-12) | 1.7(-11) | 3.2(-11) | 3.5(-12) |
| 422 | 2.5(-11) | 9.4(-12) | 8.8(-12) | 1.2(-12) | 1.1(-11) | 3.0(-11) | 3.9(-12) | 3.3(-11) | 1.8(-11) | 5.5(-12) |
| 524 | 0.0 | 2.0(-12) | 7.0(-12) | 7.5(-12) | 1.7(-11) | 7.1(-12) | 1.3(-11) | 2.8(-11) | 1.3(-11) | 2.6(-12) |
| 523 | 1.1(-11) | 1.9(-11) | 5.0(-12) | 5.7(-12) | 1.3(-11) | 1.0(-11) | 1.7(-12) | 1.2(-11) | 3.1(-11) | 3.9(-12) |
| 441 | 0.0 | 1.6(-12) | 5.6(-13) | 9.0(-13) | 6.6(-12) | 2.6(-12) | 6.7(-13) | 3.7(-12) | 5.3(-12) | 7.3(-13) |
| 440 | 2.1(-12) | 3.0(-13) | 1.1(-12) | 6.5(-13) | 2.6(-12) | 6.7(-12) | 8.2(-13) | 4.9(-12) | 3.7(-12) | 7.0(-13) |
| 542 | 0.0 | 9.4(-13) | 2.2(-12) | 9.5(-13) | 5.1(-12) | 5.4(-12) | 1.1(-12) | 7.1(-12) | 2.3(-12) | 8.9(-13) |
| 541 | 1.9(-12) | 1.4(-12) | 5.7(-13) | 1.7(-12) | 5.8(-12) | 5.2(-12) | 1.1(-12) | 2.2(-12) | 6.4(-12) | 8.5(-13) |

NOTE.—Parentheses enclose power of 10.

Astrophysical applications generally require rate constants for a thermal (i.e., Boltzmann) distribution of collision energies at a particular kinetic temperature T . Equation (8) is also applicable to generalized IOSA fundamental rates $Q(L, M, M' | T)$, which have been averaged over a Boltzmann distribution of collision energies. Because the energy separations between rotational levels are ignored in the IOSA, however, there is some ambiguity in the interpretation of the collision energy. For linear and symmetric top rotors, each of the IOSA rates corresponds uniquely to a transition into or out of the lowest level, and a prescription for interpreting the collision energy has been found for these cases which is based on the inelasticity of such transitions and which appears to give satisfactory agreement with more accurate theoretical values (Green and Chapman 1983; Chapman and Green 1984; Green 1985). For asymmetric rotors, however, eq. (8) does not lead to such a simple one-to-one correspondence between $Q(L, M, M')$ and transitions to the lowest level, and it is not entirely clear how to generalize the prescription of Chapman and Green. Furthermore, preliminary calculations on the near symmetric top HNCO (Green 1986a) suggested that this procedure may not be universally applicable. In the present study we adopt a straightforward analog of the R_{IU} definition of Chapman and Green: the IOSA energy is taken as the initial kinetic energy, eq. (8) is applied only to upward transitions, and rates for the reverse transitions are obtained from detailed balance. For transitions with small inelasticity the rate is not very sensitive to the interpretation of collision energy, and for highly inelastic transitions the rates are generally much smaller, and relatively larger errors in these can be tolerated in astrophysical applications. Nonetheless, it will be important in future studies to obtain optimal interpretation of the IOSA energy parameter and to document the reliability in general of IOSA calculations for asymmetric top rotors.

In the present study IOSA calculations were done using 32 point Gauss quadrature for θ and six-point Gauss quadrature for ϕ to obtain $Q(L, M, M')$ for 13 collision energies between 10 and 600 cm⁻¹. These were averaged over Boltzmann distributions to obtain the fundamental rates given in Table 2, which can be used with equation (8) to obtain state-to-state rate constants. Table 3 presents such rates among some of the lower levels.

III. DISCUSSION

The techniques used here have been applied to many other systems, although this is the most extensive study to date of an

asymmetric rotor. Some of the other systems have also been studied with more rigorous theoretical methods or confronted with experimental data or both. It is possible by comparison with these other studies to estimate the reliability of the current study. Probably the most extensive comparisons are available for CO (Flower and Launay 1985; Thomas, Kraemer, and Diercksen 1980), NH₃ (Green 1980b), and H₂CO (Green, Garrison, and Lester 1975). From these it appears that the worst errors come from inaccuracy of the electron gas potential. While it gives a reasonable approximation for the shape of the short-range interaction, it is incorrect in detail. Total rates (i.e., rates out of a level summed over all final levels) are given reasonably well; this is important for interpreting microwave astronomical data, as the derived number density scales with this quantity. On the other hand, the relative size of different rates may not be predicted very accurately, so these rates may not be adequate for predicting specific nonthermal population distributions such as arise, e.g., in H₂CO. It should be noted that the errors in the electron gas approximation are more severe for very low temperature collisions. On the other hand, the errors tend to mimic differences expected on going from He to H₂ and so are not entirely unwelcome. In this context, note that H₂ molecules in excited rotational levels, which may be significantly populated even below 100 K, differ from He atoms in that they support a long-range dipole-quadrupole interaction which enhances "dipole" transitions in the rotor. This effect may be included simply in the IOSA by increasing the $Q(1, 0, 0)$ rates by a factor of ~2–3.

The IOSA is expected to be quite reliable except for the lowest collision energies. Rates below ~40 K should be used with caution because of this and also because the grid of energies used here may not adequately sample the oscillations expected in low-energy cross sections. The IOSA is also problematic for highly inelastic transitions, but these generally have smaller rates, and even relatively large errors are not significant in statistical equilibrium calculations.

It is believed that the total rates presented here are accurate to ~50%. The larger individual state-to-state rates may be in error by factors of 2–3, and some of the smaller rates may only be accurate to an order of magnitude. These rates should be adequate to interpret available microwave observations to retrieve kinetic temperatures and hydrogen densities. More accurate treatments for both the intermolecular forces and collision dynamics may be desirable in the future.

This work was supported in part by NASA grant NSG 7105 to Columbia University.

REFERENCES

- Billing, G. D., and Diercksen, G. H. F. 1985, *Chem. Phys. Letters*, **121**, 94.
- Chapman, S., and Green, S. 1984, *Chem. Phys. Letters*, **112**, 436.
- Cummins, S. E., Green, S., Thaddeus, P., and Linke, R. A. 1983, *Ap. J.*, **226**, 331.
- Flower, D. R., and Launay, J. M., 1985, *M.N.R.A.S.*, **214**, 271.
- Garrison, B. J., Lester, W. A., and Miller, W. H. 1976, *J. Chem. Phys.*, **65**, 2193.
- Gordon, R. G., and Kim, Y. S. 1972, *J. Chem. Phys.*, **56**, 3122.
- Green, S. 1977, *J. Chem. Phys.*, **67**, 715.
- . 1979, *J. Chem. Phys.*, **70**, 816.
- . 1980a, *Ap. J. Suppl.*, **42**, 103.
- . 1980b, *J. Chem. Phys.*, **73**, 2740.
- Green, S. 1985, *J. Phys. Chem.*, **89**, 5289.
- . 1986a, NASA TM-87791.
- . 1986b, *Ap. J.*, **309**, 331.
- Green, S., and Chapman, S. 1983, *Chem. Phys. Letters*, **98**, 467.
- Green, S., Garrison, B. J., and Lester, W. A. 1975, *J. Chem. Phys.*, **63**, 1154.
- Green, S., Garrison, B. J., Lester, W. A., and Miller, W. H. 1978, *Ap. J. Suppl.*, **37**, 321.
- Schinke, R., Engel, V., Buck, U., Meyer, H., and Diercksen, G. H. F. 1985, *Ap. J.*, **299**, 939.
- Thomas, L. D., Kraemer, W. P., and Diercksen, G. H. F. 1980, *Chem. Phys.*, **51**, 131.

SHELDON GREEN and AMEDEO PALMA: NASA Institute for Space Studies, 2880 Broadway, New York, NY 10025